Short communication

Phenylenedimaleimide positional isomers used as lithium ion battery electrolyte additives: Relating physical and electrochemical characterization to battery performance

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HIGHLIGHTS

► The positional isomer effects of electrolyte-additive have been identified to the solid electrolyte interface (SEI) formation.
► The isomers individually provide different degrees of reduction reaction and varying SEI physical infrastructures.
► The battery performance can be attributed to the 3D construction for the SEI formation.

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ABSTRACT

This study, by using the ortho, meta, and para forms of phenylenedimaleimide (o-, m-, and p-phenylenedimaleimide), presents an analysis of electrolyte-additive positional isomer effects that are significant to the formation of the solid electrolyte interface (SEI), and thus the resulting battery's performance. The analysis is presented in terms of the SEI's electrochemical properties, growth mechanism, free volume, ionic transfer properties, and its charge–discharge performance. This study shows that the reduction reaction mechanism for each of the positional isomers is the same; however, the isomers when used individually provide different degrees of reduction reaction and varying SEI physical infrastructures. O-phenylenedimaleimide can inhibit SEI formation because its three-dimensional barrier is greater than that of either m- or p-phenylenedimaleimide. This three-dimensional barrier gives rise to a loose SEI structure that reduces ionic motion resulting in discontinuous SEI formation and a decrease in ionic diffusion velocity. Battery performance testing showed that p-phenylenedimaleimide has the greatest discharge capacity, together with significant reversibility, because of dense and uniform structure of its SEI. Our results indicate that by selecting an appropriately functionalized isomer functional groups on SEI formation and thus improve battery performance. The maleimide-based additives provide valuable information on SEI formation mechanisms for future electrolytes.

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1. Introduction

Within the lithium ion battery, the choice of any electrolyte additive(s) is crucially important to its resulting electrochemical performance. Electrolyte additives serve to reinforce the solid electrolyte interface (SEI) on the cathode's or anode's surface, and thus enhance the electrolytes overvoltage durability, while improving the battery's thermal stability and increasing the electrochemical reliability of the lithium salt [1,2].

A major issue in SEI formation on the anode's surface is that the additive needs to have strong electron-withdrawing groups with a high reduction potential. However, many studies [3] have shown that the use of cyclic carbonates e.g. propylene carbonate (PC) can have serious adverse effects, resulting largely from its intercalation into carbon electrodes where the intercalation effect leads to the separation of the sp2 layers of graphite with consequent exfoliation. In this way the crystal lattice of carbon is destroyed, additionally the

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electron-donating group, −CH₃, increases electron density within the cyclic structure, restricting electron flow and thus preventing the formation of a useful SEI [4]. Electrolyte additives have several advantages over cyclic carbonates. One of these advantages is that they lead to an electrochemical polymerization in a reduction-type SEI. The reduction-type SEI provides a better performance than the reaction-type SEI with respect to ionic transportation due to the integrity of $-C=O-$ [2] and $-C=C-$ bonding [2,5]. Due to the presence of these electron-withdrawing groups, the radical anion can be terminated by solvent molecules to form an insoluble and stable product as the preliminary SEI nuclei showing increased diffusivity with respect to lithium ions and a consequent decrease in the concentration polarization of the battery.

However, previously used electrolyte additives suffer from various problems, including gas generation [6], significant irreversibility during electrochemical reduction [7], and reduced SEI electrochemical stability in further cycles. Winter et al. [8], found that 1-fluoropropane-2-one (FA) can electrochemically react with vinylene carbonate (VC) to form a useful SEI on a carbon anode. They showed that this type of SEI produces a battery that can operate in a PC solvent. Their results indicate that the energy density of an anode half-cell, having (FA/VC) as a binary additive, has more than 360 mAh g⁻¹. In addition, Yang et al. [9], synthesized a series of solvents to investigate the effects of substituting functional groups and evaluated the resulting SEI formation on an anodic carbon surface. Their experiments showed that the modified solvent, trifluoropropylene carbonate (TFPC) with the strong electron-withdrawing group (−CF₃), can facilitate highly stable SEI formation. The intercalation potential of this solvent is also lower than that of PC. Their results also show that TFPC increases capacity and decreases irreversibility during electrochemical reaction.

To-date no studies have surveyed the effects of using specific positional isomers of electrolyte additives on SEI formation. Previously, we studied the maleimide based compounds as electrolyte additive and discover excellent performance of lithium ion battery [10]. This study uses three isomeric electrolyte additives, i.e. o-, m-, and p-phenylenedimaleimide that have the same molecular weight, but which differ in the functional substituent's position. This study also investigates positional effects on electrochemical measurements, impedance and the free volume of SEI, together with the charge–discharge performance of the battery.

2. Materials and methods

The graphite anode consisted of 93 wt% mesocarbon microbeads (MCMB-2528, Osaka Gas), 3 wt% KS-6 as a conductive additive (KS-6, Showa, Japan), and 4 wt% poly(vinylidene) fluoride (PVDF, Kureha Chemical, Japan) as a binder. The cathode material consisted of 91 wt% lithium cobalt oxide (LiCoO₂-L106 LICO Corp., Taiwan) as the active material, 5 wt% of KS-6, and 4 wt% PVDF. The electrolyte was 1.1 M lithium hexafluorophosphate (LiPF₆) in EC:PC:DEC (3:2:5 in volume) mixed solvent, 0.1 wt% maleimide-based additives were dissolved and mixed into the electrolyte. These additives were N,N′-1,4-phenylenedimaleimide (Aldrich, 98%) (p-MI), N,N′-1,3-phenylenedimaleimide (Aldrich, 98%) (m-MI), and N,N′-1,2-phenylenedimaleimide (Aldrich, 98%) (o-MI).

3. Instrumentation

The electrochemical stability of electrolytes was measured by cyclic voltammetry (CV) using a Biologic VMP3 from 3.25 to 0.01 V at a scanning rate of 0.5 mV s⁻¹. The CV measurements were made with an anode half-cell (CR2032) consisting of MCMB working, lithium metal counter electrodes (area 1.0 cm²). The electrolyte filled the space between the working and the counter electrodes.

Electrochemical impedance spectroscopy (EIS) was performed using a Biologic VMP3 in the frequency range 100 M to 0.01 Hz with an AC amplitude of 5 mV at 25 °C. All EIS measurements employed a full cell (CR2032) consisting of LiCoO₂ and MCMB electrodes (area 1.0 cm²). The electrolytes filled the space between the LiCoO₂ and the MCMB electrodes. Riveted refinement of the equivalent circuit model was used to simulate and demonstrate the physical meanings of the semicircles in the EIS spectra. R_1 is defined as the electrolyte resistance, R_2 is the bulk resistance of the SEI, and R_3 is the contact resistance between the SEI and the electrode's surface.

The Doppler-broadening S parameter was investigated using typical positron annihilation spectroscopy (PAS) with a slow positron beam setup. A ²²Na radioactive source with an original strength of 50 mCi was deposited on a nickel foil. The source was placed approximately 3 m from the Ge detector. All the Doppler-broadening S parameter measurements were performed using an MCMB anode disassembled from a full cell (CR2032) which was charged to 4.3 V and discharged to 2.75 V in advance. After discharging, the anode electrode was washed three times in dimethyl carbonate (DMC). This step was performed to confirm that the lithium salt, did not affect the sample surface detection in Doppler-broadening PAS measurements. After this treatment, the samples were fixed on a detecting board with a sample-detector distance of 3–4 cm. The sample preparation steps for the PAS measurement followed those in our previous paper [11].

To determine the resulting performance, batteries with the additives were constant current (CC) charged at 0.2 C and discharged at 0.2 C (Maccor Battery Tester series 4000).

4. Results and discussion

Fig. 1a shows cyclic voltammogram measurements for the anode half-cells made to include the positional isomers of phenylenedimaleimide (MI). According to the enlarged picture in Fig. 1a, the three phenylenedimaleimide (MI) additives show similar reduction potential locates at 2.4–2.7 V and the similar current density response, indicating the reduction reaction mechanism of MIs are the same. In addition, Fig. 1a also demonstrates a similar reduction tendency for lithium ion intercalating into MCMB. However, the starting time of intercalation is delayed when the 3D barrier structure of the additive increases. For example, the intercalation potential of the electrolyte with p-MI begins at 0.38 V and the electrolyte with m-MI (o-MI) stems from 0.32 V (0.28 V). The observed current density response indicates that the scan current (I_P) of o-MI is considerably smaller than other additives, regardless of cathodic or anodic reactions. These results show that the intercalation process cannot easily proceed when the electrolyte contains o-MI. Therefore, the sequence of the I_P intensities is p-MI > m-MI > o-MI. In addition, the integral area of the cathodic reaction in the range from 3.3 to 0.01 V demonstrates the relative amount of columbic electrons involved in the intercalation process. According to the table in Fig. 1a, the columbic value of p-MI is 27.621 C cm⁻², which is higher than m-MI (20.192 C cm⁻²) and o-MI (13.573 C cm⁻²). Under the same conditions, the anodic reaction represents the columbic value of electrons for the de-intercalation process of LiC₆ to lithium ions after SEI formation: the irreversible capacity of cathodic and anodic reaction for p-MI is 8.95%, which is lower than that for m-MI (10.9%) and o-MI (15.1%). This analysis shows that the additive with a para position functional group is sufficient for SEI electrochemical formation and the intercalation reaction. The uniform distribution of SEI formation facilitates lithium ion diffusion and decreases battery polarization. Furthermore, the columbic depression between the cathodic and anodic reactions among the three additives shows that the p-MI consumes
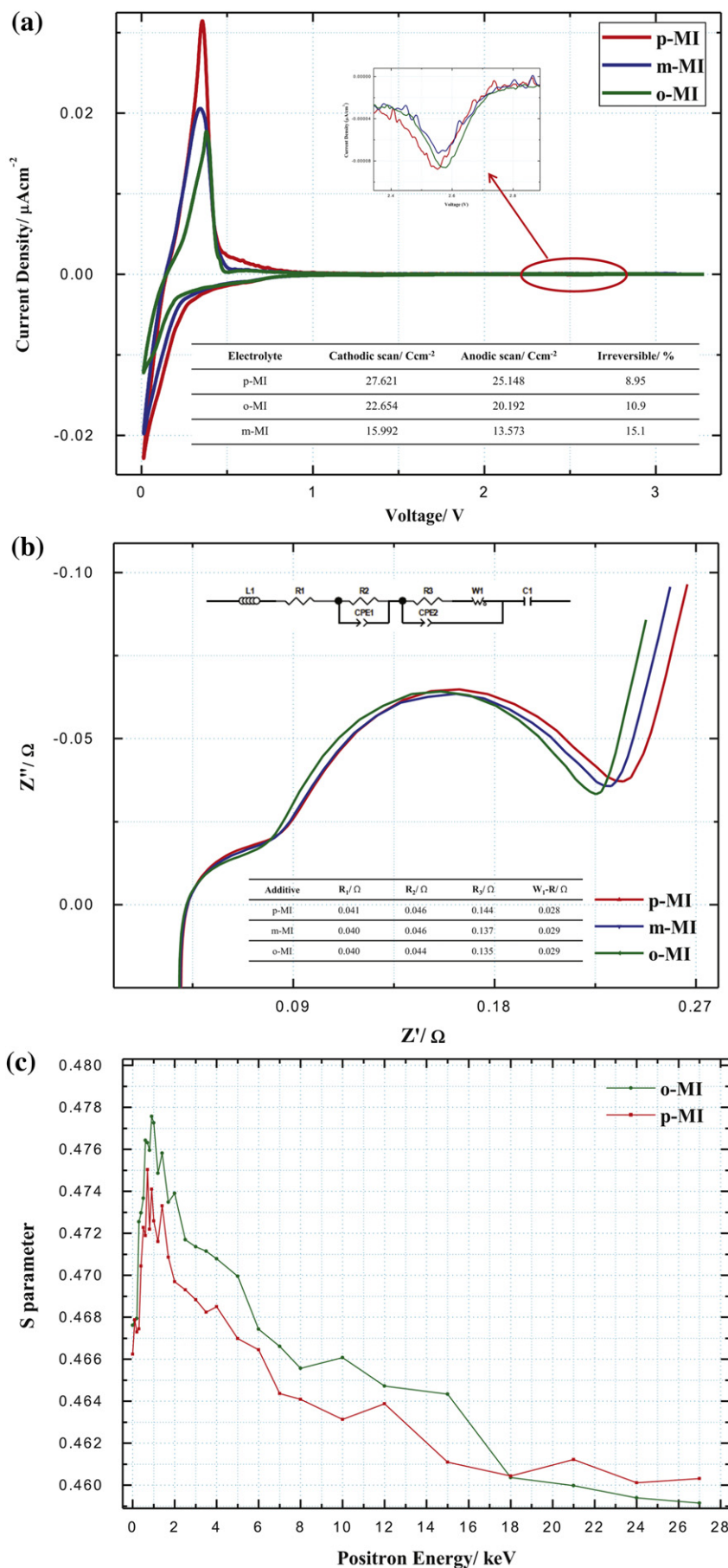
(a)

Electrolyte	Cathodic scan/ Ccm^{-2}	Anodic scan/ Ccm^{-2}	Irreversible/ %
p-MI	27.621	25.148	8.95
o-MI	22.654	20.192	10.9
m-MI	15.992	13.573	15.1

(b)

Additive	R$_1$/ Ω	R$_2$/ Ω	R$_3$/ Ω	W$_1$-R/ Ω
p-MI	0.041	0.046	0.144	0.028
m-MI	0.040	0.046	0.137	0.029
o-MI	0.040	0.044	0.135	0.029

(c)

Fig. 1. (a) Cyclic voltammograms of lithium plating/stripping on the stainless steel electrode for the electrolytes with MIs additives are shown. Working and counter electrode, stainless steel; reference electrode, lithium; scan rate = 0.5 mV s^{-1}. (b) Impedance spectra of LiCoO$_2$/MCMB full cell after 1st battery formation. Schematic representation of the item of equivalent circuit inside the LiCoO$_2$/MCMB battery has been arranged inside the figure. (c) S energy profiles measurements of LiCoO$_2$/MCMB full cell with MIs additives.

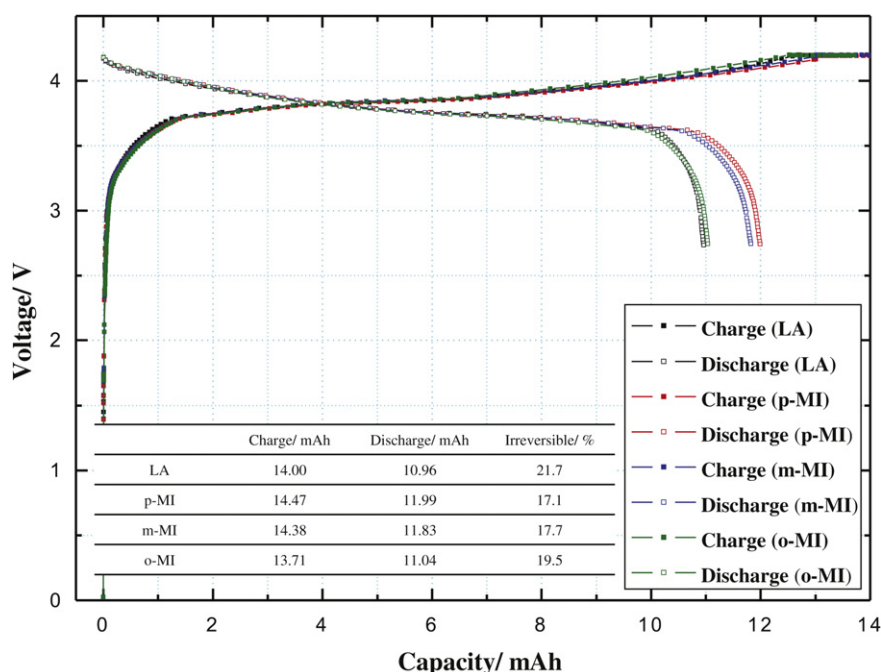|	Charge/ mAh	Discharge/ mAh	Irreversible/ %
LA	14.00	10.96	21.7
p-MI	14.47	11.99	17.1
m-MI	14.38	11.83	17.7
o-MI	13.71	11.04	19.5

Fig. 2. The 1st charge and discharge profile of LiCoO$_2$/MCMB full cell at current of 0.2 C.

2.473 C cm^{-2} of columbic electrons for SEI formation, which is similar to m-MI (2.462 C cm^{-2}) and o-MI (2.419 C cm^{-2}).

This evidence shows that the positional isomers of maleimide-based additives have the same reduction reaction mechanism, the only difference being the density and distribution of SEI resulting from the 3D structural barrier.

Fig. 1b shows the EIS measurements for a full cell using three types of isomer electrolyte additives. According to this spectrum, the simulated values of the resistance (R_1) of the electrolyte and the resistance (R_2) of the bulk SEI are extremely similar, indicating that isomeric additives do not affect the ionic conductivity of the electrolyte and the chemical composition of the bulk SEI. However, R_3 greatly varies among the three additives, indicating that R_3 is the charge transfer resistance (R_{ct}) on both cathode and anode. According to the table in Fig. 1b, the p-MI electrolyte achieves an R_3 value of 0.144 Ω, which is slightly larger than o-MI (0.135 Ω). Thus, the effect of the 3D structure of SEI affects the contact impedance between the electrode and the SEI. In the SEI growth process, when the electrochemical reduction proceeds, adding p-MI can fabricate a dense, high uniformity of SEI. This is because the angular distance of the two MI groups is nearly 180°, which can polymerize with each other, in a facile manner, thus restricting the surface area on most of MCMB and tiny of LiCoO$_2$. Without the dimensional barrier, the benefit of the para position assists the chain reaction of SEI formation. However, the o-MI additive has a smaller (~60°) angular distance, leading a loose, discontinuous of SEI formation. This loose and porous SEI structure easily soaks up the electrolyte as it flows to the electrode, and the R_3 of o-MI is therefore slightly smaller than that of p-MI, duo to the SEI impedance being purely resistive, an increase in its density results only in a shift of the semi-circle along the real axis of EIS spectrum.

However, the SEI not only dramatically slows the kinetics of electrolyte decomposition but also reduces active lithium consumption between the lithiated carbon electrode and the electrolyte. Therefore, we can conclude that when all the available surface area is uniformly coated with SEI film, further decomposition of electrolyte ceases [12].

Fig. 1c illustrates that the S parameter shows several obvious transition layers. The layers visible at 0.497, 0.698, 0.911, and 1.405 keV display the nano hole of the bulk SEI. However, the S energy profile from 2.493 to 17.94 keV becomes horizontal and smooth, indicating the lack of a clear transition layer which reveals no other solid layer formation occurs; thus, the electrolyte only exists between the SEI and the electrode's surface. In Fig. 1c, we see that the SEI formed from the o-MI additive provides nearly 5%—6% of S parameter, i.e. greater than p-MI, indicating a higher free volume. Therefore, the PAS measurements indicate the formation, using o-MI, of a loosely structured SEI. Conversely, using p-MI leads to a high density SEI with a reduced free volume. These results confirm the previous EIS measurements.

Fig. 2 shows the battery performance obtained by analysing the significance of isomeric additive substituent positional effects. The charge—discharge curve shows that the electrolyte with the p-MI additive possesses the highest discharge capacity (11.99 mAh) and the minimum irreversibility (17.1%) at first cycle. In addition, the discharge capacity of the battery decreases as the 3D construction of the SEI increases, such as m-MI (11.83 mAh) and o-MI (11.04 mAh). These results show that it is not only essential to design the appropriate chemical composition of electrolyte additive for SEI formation, but it is also necessary to focus on the ionic transfer properties of the SEI. Conversely, regardless of the open circuit potential (OCP) of the discharge and charge—discharge plateaus, the three isomer additives have almost the same battery performance. The above data, taken together, indicates that selective maleimide-based compounds are excellent electrolyte additives for improving the performance of the SEI.

5. Conclusion

This study uses MI-based additives with different positional isomers to investigate interesting aspects of SEI formation. The 'battery capability' of these isomers follows the order p-MI > m-MI > o-MI. This performance can be attributed to the critical benefits of the para position functional group in promoting an

enhanced 3D construction for the SEI, with a higher density and a reduced free volume, through electrochemical reduction, whereas using the additive having the ortho position substituent leads to the opposite outcome. This study discusses the additive electrochemical reaction, SEI formation, the SEI intrinsic structure, and battery performance. Our results indicate that MI has an excellent SEI formation capability if the para functionalized substituent is selected. A suitable SEI formed by the p-MI additive derivatives shows the uniform distribution effects of ionic transport factors on SEI formation. This in turn assists lithium ion diffusion, which decreases the redox irreversibility and capacity increment. Future research will be directed towards investigating electrolyte additives with different functional groups. Such functionalized maleimide-containing chains are being synthesized to allow further extensive study.

Acknowledgement

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